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US 4187287	US 3867557
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(54) Stabilising dentifrices containing aldehyde flavours

(57) Dentifrices with stability against discolouration upon aging contain as flavouring agent cinnamic aldehyde or citral and 0.1-5% of (1) a terpene or sesquiterpene colour stabilizer with trisubstituted double bonds e.g. limonene, ocimene, caryophyllene, citrus oils, clove sesquiterpenes, myrcene, terpene derivatives, citronellyl acetate or (2) propylene glycol or dipropylene glycol in a dental vehicle of pH below 8.5 and free of oxidizing agents.

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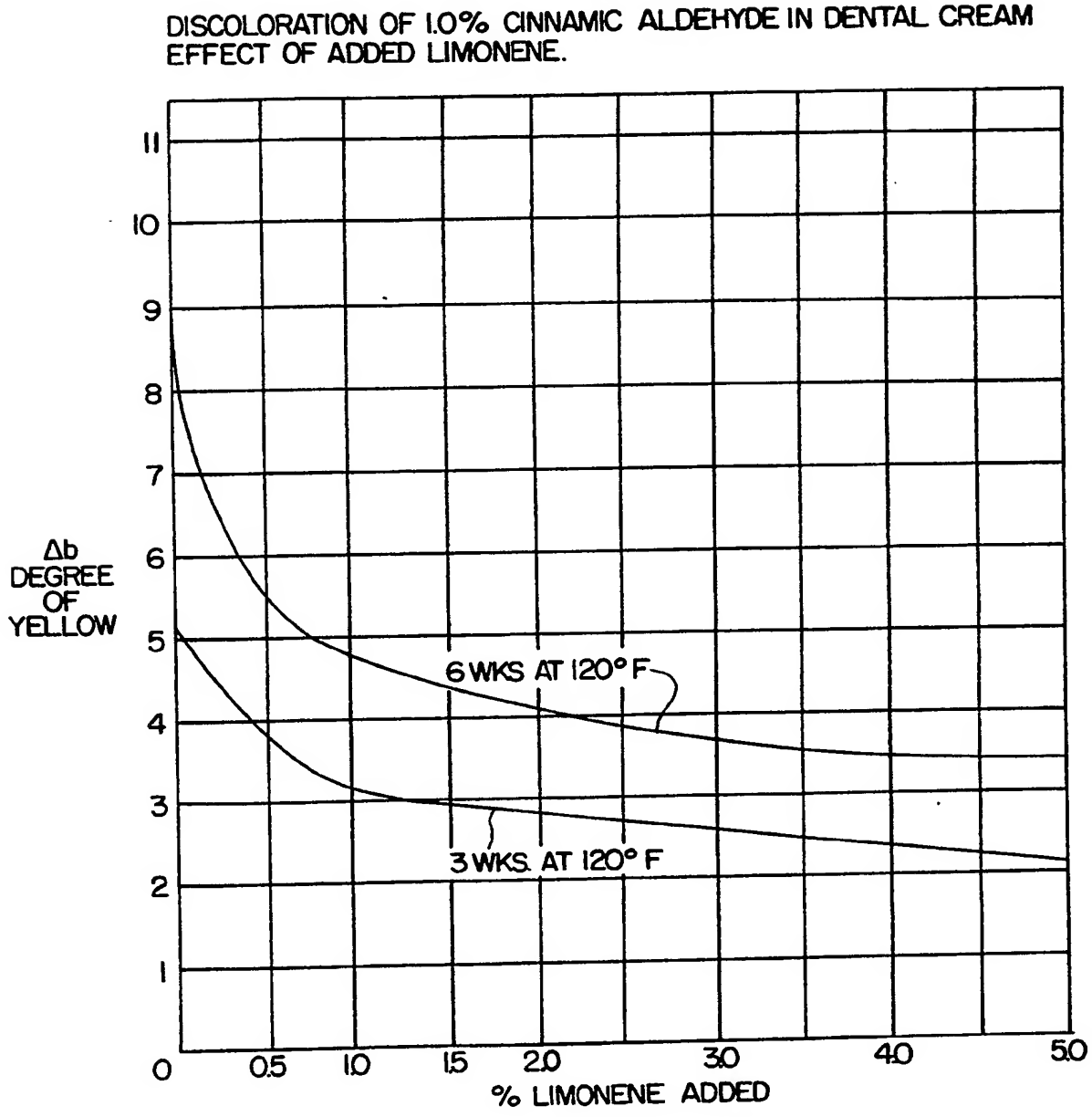
FIG. 1.



SPECIFICATION

Stabilising of cinnamic aldehyde-containing flavours with terpenes and sesquiterpenes and propylene glycol and dipropylene glycol

The present invention relates to a colour-stabilised dentifrice composition comprising a cinnamic aldehyde or citral flavourant which is subject to discolouration/yellowing upon ageing, and a trisubstituted double bond-containing terpene or sesquiterpene or propylene glycol which significantly reduces and/or prevents discolouration, and maintaining the pH of the said composition below 8.5 and preferably at a neutral to acid pH. The dentifrice may be aqueous or anhydrous. The dentifrice must be free of oxidising agents such as hydrogen peroxide, or salts delivering hydrogen peroxide such as sodium perborate, peracids and salts of peracids.

The prior art is replete with dental formulations comprising the combination of a cinnamic aldehyde or citral flavourant and a terpene as shown in U.S. Patent Nos. 3,867,557 and 3,928,560 wherein oral compositions containing 0.0001-20% paramethoxycinnamaldehyde flavouring agent is dissolved in 100 parts orange oil (Example VII), and 4% of the cinnamaldehyde is dissolved in 500ml ethyl alcohol and 10 ml orange (Example XIII). Essential oils such as orange oil are known to contain terpenes. U.S. Patent No. 4,001,438 also discloses flavour formulations containing citral and orange terpenes (Example B in column 10) to be used in oral compositions. However, there is no recognition in this group of patents of the discolouration or yellowing problem associated with the use of the cinnamic aldehyde flavourant. These patents relate to different aspects in dentifrice formulations. The disclosure of the combination of cinnamic aldehyde flavourant and a terpene is incidental to a general discussion of flavourants.

The prior art is replete with dental formulations comprising the combination of a cinnamic aldehyde or citral flavourant and propylene glycol or dipropylene glycol as shown in U.S. Patent Nos. 3,867,557 and 3,928,560 wherein oral compositions containing 0.0001-20% paramethoxycinnamaldehyde flavouring agent is dissolved in 100 parts propylene glycol; U.S. Patent No. 4,132,771 and U.S. Patent No. 4,187,287, wherein a two-tone flavoured dentifrice containing cinnamon flavour is in a propylene glycol vehicle; U.S. Patent No. 4,242,323 wherein a plaque inhibiting oral composition containing cinnamon oil flavourant also utilises propylene glycol as the liquid vehicle; and U.S. Patent No. 3,864,472 relating to a clear lemon-flavoured mouthwash containing lemon oil, cinnamic aldehyde and glycerine or propylene glycol. U.S. Patent No. 4,001,438 also discloses flavour formulations comprising citral and/or cinnamic aldehyde as a component in a physically entrapped flavour composition which is admixed with a non-confined flavour oil, a suspending agent and preferably a small amount (0.5%) of propylene glycol which improves product stability (column 6, lines 32-33), useful in oral compositions. However, there is no recognition in this group of patents of the discolouration or yellowing problem due to ageing associated with the use of the cinnamic aldehyde flavourant. These patents relate to different aspects in dentifrice formulations. The disclosure of the combination of cinnamic aldehyde flavourant and propylene glycol is incidental to a general discussion of flavourants and typical humectants.

The prior art also recognised the fading and/or deterioration of flavours or dyes as shown in U.S. Patent No. 3,666,496 wherein a poly-(oxyethylene)-poly(oxypropylene) copolymer is added to terpene containing flavours such as orange oil to prevent deterioration of the flavour to be used in flavoured foods or beverages. U.S. Patent No. 4,305,928 addes 0.05-5% phytic acid and/or benzoic acid as a chelator to prevent or reduce colour fading of red or yellow monazo or blue triarylmethylene dye-coloured visually clear dentifrice. U.S. Patent No. 3,957,964 discloses a dentifrice containing encapsulated flavouring which includes oil of cinnamon or orange and is kept separate from the dentifrice base (which may include propylene glycol) during storage until released when the dentrifice is used, thereby providing a more stable and fresher tasting flavoured dentifrice. However, there is no mention in the aforesaid patents of the stabilisation of the cinnamic aldehyde or citral flavour with a specific group of terpenes or sesquiterpenes characterised by a trisubstituted double bond or with propylene glycol or dipropylene glycol.

U.S. Patent No. 2,184,526 also recognised the instability against oxidisation by air of p-isopropyl-methylhydrocinnamic aldehyde as a perfume ingredient, wherein the aldehyde is converted into the corresponding acid, thereby destroying the aldehyde odour. The addition of alcohols of the aromatic or terpene series stabilises the aldehyde against air oxidisation, by converting the aldehyde into a hemi-acetal of the said alcohol.

U.S. Patent No. 3,671,630 discloses the use of multiple classes of terpenes as colour stabilisers for aqueous halogenated phenolic germidical compositions which discolour within a few hours of exposure to light. However, many terpenes such as limonene have been disclosed to be ineffective. The halogenated phenolic germicidal compounds cannot be equated to the cinnamic aldehyde or citral flavourants which are unsaturated aldehydes. In addition, it is noted that limonene, one of the terpenes specifically used as a colour stabiliser for the flavourant, is specifically excluded as inneffective in stabilising the germicidal composition.

None of the above cited art discloses the use of a specific group of terpenes or sesquiterpenes in a dentifrice, free of oxidising agents and maintained at an acid or neutral pH, containing the cinnamic aldehyde or citral flavour, to reduce discolouration of the said flavourant upon ageing.

It has unexpectedly been found that discolouration on ageing of dentifrice products that are flavoured with

cinnamic aldehyde or citral can be reduced and/or prevented by the addition of (1) a terpene or sesquiterpene characterised by trisubstituted double bonds which may be selected from the group consisting of limonene and essential oils rich in limonene, ocimene, caryophyllene and clove sesquiterpene, myrcrene, derivatives of said terpenes and mixtures thereof or (2) of propylene glycol or dipropylene glycol or mixtures thereof. It is essential that the dental vehicle be free of oxidising agents and be maintained at an acid to neutral pH for the said terpenes and sesquiterenes to function effectively.

The present invention aims to provide dentifrice formulations containing cinnamic aldehyde or citral flavour that do not turn yellow or discolour with age or have a lesser tendency to do so.

The present invention also aims to provide a colour stabilized dental cream or mouthwash comprising cinnamic aldehyde or citral flavour and an effective amount of a colour stabilizer comprising propylene glycol or dipropylene glycol or mixtures thereof or a compound characterized by trisubstituted double bonds and selected from the group consisting of limonene and essential oils rich in limonene, ocimene, caryophyllene and clove sesquiterpenes, myrcene and terpene derivatives thereof.

The present invention also aims to provide a colour stabilized cinnamic aldehyde or citral containing dentifrice maintained at a pH below 8.5, and preferably at a neutral to acid pH.

The present invention also aims to provide an acid or neutral colour stabilized aldehyde flavourant-containing dentifrice free of oxidizing agents.

The present invention also aims to provide a colour stabilized white dental cream or mouthrinse containing cinnamic aldehyde or citral flavourant.

According to the present invention a dentifrice which has improved stability against discolouration upon aging, comprises an unsaturated aldehyde containing flavourant selected from the group consisting of cinnamic aldehyde and citral which is subject to discolouration upon ageing, and about 0.1-5% by weight of (1) a terpene or sesquiterpene colour stabilizer characterized by trisubstituted double bonds and preferably selected from the group consisting of limonene and essential oils rich in limonene, ocimene, caryophyllene and clove sesquiterpenes, myrcene, terpene derivatives thereof, and mixtures thereof, or (2) propylene glycol, dipropylene glycol and mixtures thereof, in a dental vehicle free of oxidizing agents and maintained at a pH below 8.5, and preferably at an acid to neutral pH of about 5-7.5.

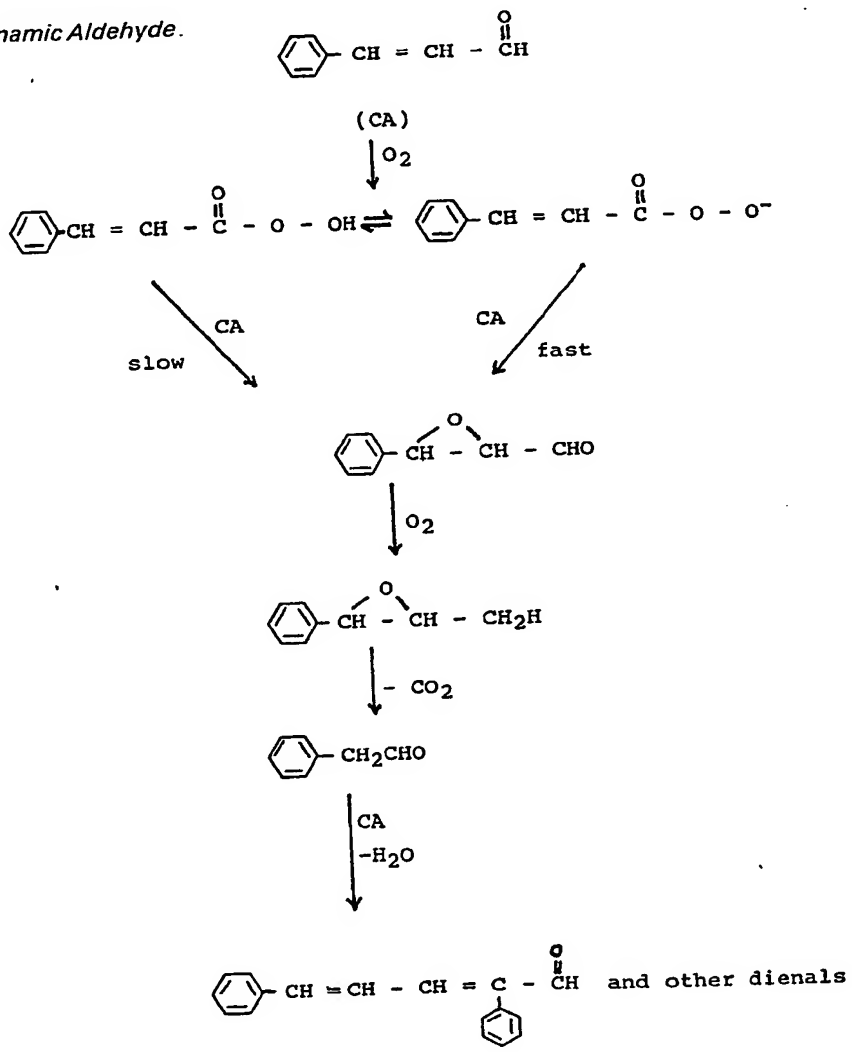
More specifically, the present invention relates to a colour stabilized white dental cream or mouthwash, free of oxidizing agents and having an acid to neutral pH comprising about 0.1-1% by weight of cinnamic aldehyde or citral flavourant and (1) one or more terpenes or sesquiterpenes containing trisubstituted double bonds or (2) propylene glycol or dipropylene glycol as the discolouration inhibitor, preferably in a 1:1 proportion.

It has been found that the cinnamic aldehyde or citral flavourant decompose upon ageing to form conjugated unsaturated aldehydes (dienals). These dienals are responsible for the yellowing or discolouration evident with cinnamic aldehyde or citral in white dental products which include liquids or creams (pastes).

Commercial dental creams utilizing low levels of cinnamic aldehyde have circumvented the discolouration problem by colouring the product, e.g. red, blue, light green, etc. However, in white dental creams, the discolouration from a low level of cinnamic aldehyde is unacceptable.

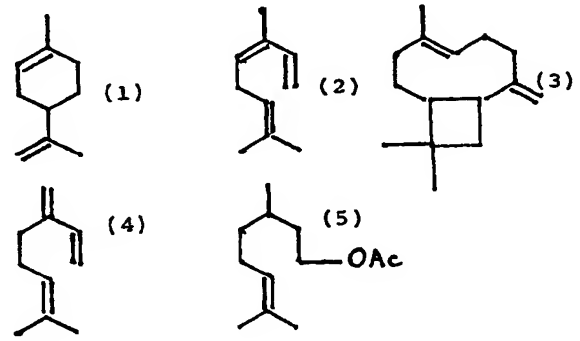
The autoxidation of cinnamic aldehyde (CA) proceeds according to the following mechanism:

Autoxidation of Cinnamic Aldehyde.



The acid forms even when samples are stored in tightly capped bottles with the head space flushed with nitrogen. Cinnamaldehyde is quite sensitive to small amounts of oxygen. Since cinnamic acid is white, its formation, which occurs within a short time after exposure, is not responsible for the yellowing of cinnamaldehyde. The intensity of the yellow colour increases with time of oxygen exposure, rather than with the quantity of oxygen, indicating that more complex oxidation occurs during aging. Specifically, the formation of conjugated dienals are the intensive yellow components responsible for the discolouration and yellowing of the cinnamic aldehyde.

It has now been found that discolouration from low levels of cinnamic aldehyde (a maximum of about 1% by weight) is reduced when certain terpenes or sesquiterpenes with trisubstituted double bonds are incorporated into the dentifrice composition, preferably in a 1:1 weight ratio. The terpenes include limonene (1), ocimene (2), caryophyllene (3), myrcene (4), terpene derivatives such as citronellyl acetate (5), and mixtures thereof.



Each individually at 1:1 proportions with cinnamic aldehyde significantly reduced cinnamic aldehyde discolouration on aging in a glass bottle. These compounds also reduce yellowing on aging in white dental cream, as shown in Table 6A, wherein a 40% reduction in yellowing is effected. Natural products containing these compounds can be used, such as essential oils rich in limonene, which include citrus oils such as orange, grapefruit, tangerine and mandarin oils. Clove sesquiterpenes are also effective colour stabilizers.

The dental base utilized in the present invention may be in the form of a paste, cream or liquid mouthwash, comprising known ingredients conventionally used in the dentifrice art.

Paste or cream dentifrices may be based on aqueous or substantially non-aqueous systems. The former will usually include substantial proportions of finely divided, solid polishing agent, surface active agent, gelling agent, water and some non-aqueous vehicle, e.g. glycerol, sorbitol, and will be opaque, whereas the latter type will often be a clear gel or opaque containing a minor proportion of a visually clear particulate solid polishing agent, a larger proportion of non-aqueous vehicle, which may comprise at least 10% of the formulation of propylene glycol or dipropylene glycol solely or admixed with other non-aqueous liquid vehicles, such as sorbitol or glycerine, surface active agent and gelling agent, with a minor proportion of water often being present.

The surface active agent, or detergent, present in the dentifrice may sometimes be cationic or amphoteric but will usually be anionic or nonionic. Of these compounds, the anionics are the most preferred. The anionic detergents or surface active agents also usually serve as foaming agents. Among the useful anionic detergents may be mentioned the higher fatty acid monoglyceride monosulphates, such as the sodium salts of the monosulphated monoglycerides of hydrogenated coconut oil fatty acid; higher alkyl sulphates, such as sodium lauryl sulphate; higher alkyl aryl sulphonates, such as sodium linear dodecyl benzene sulphonate; higher olefin sulphonates, such as sodium higher olefin sulphonate in which the olefin group is of 12 to 21 carbon atoms; higher alkyl potassium sulphoacetates; higher fatty acid esters of 1,2-dihydroxypropane sulphonates, magnesium salt; the substantially saturated higher aliphatic acyl amides of lower aliphatic aminocarboxylic acid alkali metal salts, such as those having 12 to 16 carbon atoms in the fatty acyl radicals, higher alkyl poly-lower alkoxy (of 10 to 100 alkoxies) sodium sulphates; higher fatty acid sodium and potassium soaps of coconut oil and tallow, and the like. As is noted, most frequently the detergents are sulphated or sulphonated compounds. Examples of useful anionic amides which may be employed are N-lauroyl sarcosine and the sodium, potassium and ethanolamine salts of N-lauroyl, N-myristoyl- and N-palmitoyl sarcosines. In the above descriptions, "higher" refers to chain lengths of 12 to 22 carbon atoms, preferably of 12 to 16 carbon atoms. Lower means 2 to 4 carbon atoms, preferably 2 to 3 carbon atoms and most preferably, two carbon atoms.

The nonionic detergents include those containing chains of lower alkylene oxide, e.g. ethylene oxide or propylene oxide, in which there are present from 10 to 100 or more moles of lower alkylene oxide. Among such materials are the block copolymers of ethylene oxide, propylene oxide and propylene glycol, sold under the mark Pluronics (Registered Trade Mark); the alkyl phenyl polyethoxy ethanols, sold under the mark Igepal (Registered Trade Mark); mixed copolymers of ethylene oxide and propylene oxide sold under the mark Ucon (Registered Trade Mark); and various other well known nonionics derived from fatty alcohols or acids and polyethylene oxide. The amphoteric or ampholytic agents include long chain (alkyl) amido-alkylene-alkalated amine derivatives, such as those sold under the mark Miranol (Registered Trade Mark), e.g. Miranol C_2M; and cationic germicidal detergents, such as diisobutyl-phenoxyethoxyethyl dimethyl benzyl ammonium chloride; benzyl dimethyl stearyl ammonium chloride; and tertiary amines having a higher fatty alkyl group and two polyoxyethylene groups attached to the nitrogen thereof.

The detergents constitute about 0.5-5% and preferably up to 3% by weight of the dentifrice composition.

Toothpastes, dental creams and toothpowders conventionally contain substantially water insoluble polishing agents or abrasives which are compatible with the formulation, in amounts from about 20-75% by weight of the total cream or paste formulation and up to 95% in toothpowders. Suitable polishing agents include anhydrous dicalcium phosphate, dicalcium phosphate dihydrate, tricalcium phosphate, insoluble sodium metaphosphate, crystalline silica, colloidal silica, complex aluminosilicates, aluminium hydroxide (including alumina trihydrate or hydrated alumina), magnesium phosphate, magnesium carbonate, calcium carbonate, calcium pyrophosphate, bentonite, talc, calcium silicate, calcium aluminate, aluminium oxide, aluminium silicate, and silica xerogels. Most of the polishing agents mentioned are most useful in the preparation of opaque dentifrices but some of them, such as the colloidal silicas, especially the silica zerogels, and complex sodium aluminosilicates, may be utilized in the manufacture of clear dentifrices, because their indexes of refraction approximate to those of the rest of the dentifrice constituents in an appropriate vehicle.

In dental cream or toothpaste dentifrice formulations, the liquids and solids should necessarily be proportioned to form a creamy mass of desired consistency which for example is extrudable from a collapsible aluminium tube. In general, the liquids in the dental cream will comprise chiefly water, glycerine, sorbitol, polyethylene glycol, or propylene glycol 400, including suitable mixtures thereof. It is advantageous usually to use a mixture of both water, and a humectant such as glycerine, or sorbitol or mixtures thereof. The total liquid content will generally be about 20-75% by weight of the formulation. It is preferred to use also a gelling agent in dental creams such as the natural and synthetic gum-like materials, e.g. Irish Moss, gum tragacanth, sodium carboxymethylcellulose, polyvinylpyrrolidone, or starch. Irish Moss and sodium carboxymethylcellulose, are compatible particularly and are preferred gelling agents. The gum content is

usually in an amount up to about 10% and preferably about 0.3-5% by weight of the formulation. Fillers such as pyrogenic silica and silica aerogel may also be used, typically in amounts up to about 10% by weight to supplement the gelling agent. These colloidal silica aerogels which include those sold under the mark Syloid, e.g. Syloid 244 (Registered Trade Mark), Syloid 266 (Registered Trade Mark) and Aerosil (Registered Trade Mark), and the pyrogenic silica sold as Cab-O-Sil (Registered Trade Mark) may be used as gelling and thickening agents.

The liquid vehicle in the form of a mouthwash usually includes ethyl alcohol, glycerine, sorbitol, water and mixtures thereof, in an amount of about 90-98% total liquid content by weight.

Various other materials may also be incorporated into the dental vehicle. Examples thereof are fluorine-containing compounds such as stannous fluoride, potassium stannous fluoride (SnF_2KP), sodium hexafluorostannate, stannous chlorofluoride, sodium fluorozirconate and sodium monofluorophosphate. These materials, which dissociate or release fluorine-containing ions in water, may be present in the dental vehicle in an effective, but non-toxic amount, usually within the range of about 0.1-5% by weight. Other additives include preservatives such as sodium benzoate, chlorophyll compounds, silicones, ammoniated materials such as urea and diammonium phosphate, antibacterial agents such as benzethonium chloride and other quaternary antibacterial compounds, sweeteners such as sodium saccharin, blue dyes, additional flavours, such as peppermint or spearmint and the like. These additives may be used in amounts which do not adversely affect the properties and characteristics of the dentifrice in accordance with the present invention. Each constituent may be present in minimal amounts of up to a maximum of 5% by weight and preferably up to 1% by weight of the formulation.

The dentifrice of the present invention is prepared by conventional methods of making toothpaste, dental creams, mouthwashes and toothpowder. More specifically, a toothpaste may be prepared by forming a gel with carboxymethylcellulose and water, adding thereto with mixing the powdered materials and humectant, followed by the addition with mixing of polishing agent and then the surfactant and the flavour together with the terpene or sesquiterpene colour stabilizer, and inserting the final mixtures in tubes. The flavour composition is preferably blended with the terpene or sesquiterpene colour stabilizer prior to addition to the mixture.

In the practice of the present invention to promote oral hygiene, the dentifrice according to the present invention is applied regularly to dental enamel by brushing the teeth for 30-90 seconds at least once daily and/or rinsing the teeth with a mouthwash once daily.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples, and the accompanying Figure which plots the amount of limonene added to a dental cream containing 1.0% cinnamic aldehyde against the yellowing of the dental cream.

The examples are illustrated of the nature of the present invention, but it is to be understood that the invention is not limited thereto. The compositions are prepared in the usual manner and all amounts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated. The flavour ingredient is a cinnamic aldehyde- or citral-containing flavourant composition, to which a terpene or sesquiterpene (Tables 1 to 4) or propylene glycol or dipropylene glycol is added as described in the experiments following the examples (Table 5).

Examples 1A and 1B

Dental creams having the compositions shown below are made up:

Ingredients	*A* %	*B* %
Glycerine	22.00	22.0
Sodium Monofluorophosphate	0.76	0.8
Sodium Carboxymethylcellulose	1.00	1.0
Tetrasodium Pyrophosphate	0.25	0.2
Sodium Saccharin	0.20	0.2
Sodium Benzoate	0.50	0.5
Deionized Water	24.49	24.5
Dicalcium Phosphate Dihydrate	48.76	48.8
Flavour	0.84	0.8
Sodium Lauryl Sulphate	1.20	1.2
pH	6.9-7.1	6.9-7.1

Examples 2A and 2B

Dental creams having the compositions shown below are made up:

Ingredients	*A* %	*B* %
Glycerine	10.00	10.0
Sodium Monofluorophosphate	0.76	0.8
Sodium Carboxymethylcellulose	1.10	1.1
Sodium Benzoate	0.50	0.5
Sodium Saccharin	0.20	0.2
Sorbitol (70% Aqueous Solution)	17.00	17.0
Deionized Water	22.19	22.2
Titanium Dioxide	0.40	0.4
Insoluble Sodium Metaphosphate	39.35	39.3
Hydrated Alumina	1.00	1.0
Anhydrous Dicalcium Phosphate	5.00	5.0
Flavour	1.00	1.0
Sodium Lauryl Sulphate	1.50	1.5
		6.15 pH

Example 3

A gel dental cream having the composition shown below is made up:

Ingredients	%
Deionized Water	3.00
Sodium Saccharin	0.30
Sodium Monofluorophosphate	0.76
Glycerine	25.00
Sodium Carboxymethylcellulose	0.35
Sodium Benzoate	0.50
Titanium Dioxide	0.01
Sorbitol (70% Aqueous Solution)	41.53
Carbowax 660 (PEG 12)	3.00
Colour	0.20
Sodium Alumino-silicate (silica containing combined alumina)	18.00
Colloidal Silica Aerogel	5.50
Flavour	0.65
Sodium Lauryl Sulphate	1.20

Example 4

A toothpaste having the composition set out below is made up:

Ingredients	%
Glycerine	25.00
Sodium Carboxymethylcellulose	1.40
Sodium Benzoate	0.50
Sodium Saccharin	0.20
Sodium Monofluorophosphate	0.76
Deionized Water	35.44
Titanium Dioxide	0.40
Aluminium Oxide	10.00
Silica	24.00
Flavour	1.10
Sodium Lauryl Sulphate	1.20
pH 6.2 ± 0.5	

Example 5

Example 4 is repeated except that the sodium lauryl sulphate is increased to 1.5% and the water content adjusted accordingly.

Example 6

A mouthwash having the composition set out below is made up:

Ingredients	%
Ethyl Alcohol	15 - 30
Glycerine	10 - 15
Polysorbate 80[1]	2 - 3
Poloxamer 338[2]	0 - 0.5
Benzethonium Chloride	0 - 0.075
Flavour Composition	0.1 - 0.5
Deionized Water	Balance

Notes

[1] A mixture of oleate esters of sorbitol and sorbital anhydrides, consisting of the monoester condensed with approximately 20 moles of ethylene oxide.

[2] The polyoxyethylene polyoxypropylene block polymer that conforms to the formula:

$$HO(CH_2CH_2O)_x\left(-CH(CH_3)-CH_2O\right)_y(CH_2CH_2O)_zH,$$

wherein x and z = 128, and y = 54.

Flavour levels in mouthwash are generally less than in a dental cream.

Example 7

Dental powders having the compositions set out below are made up:

Ingredients	*A* %	*B* %
Magnesium Silicate	7.00	7.00
Sodium Saccharin	0.15	0.2
Flavour	2.50	2.5
Dicalcium Phosphate-Anhy.	88.35	88.3
Sodium Lauryl Sulphate	2.00	2.0

Flavour levels in dental powders are generally greater than in dental creams.

Example 8

A non-aqueous dental cream having the composition set out below was made up:

Ingredients	%
Propylene Glycol	43.4
Klucel GF[1] (Hercules)	1.5
Sodium Saccharin	0.2
TiO_2	0.4
Dicalcium Phosphate Dihydrate	50.0
Peroxydiphosphate	3.0
Sodium Lauryl Sulphate	1.5
pH 6.4	

Notes

[1] Hydroxypropyl cellulose - a propylene glycol ether of cellulose.

Example 9

An aqueous dental cream having the composition set out below is made up:

Ingredients	%
Propylene Glycol	22.0
Sodium Monofluorophosphate	0.8
Sodium Carboxymethylcellulose	1.0
Tetrasodium Pyrophosphate	0.2
Sodium Saccharin	0.2
Sodium Benzoate	0.5
Dicalcium Phosphate Dihydrate	48.8
Spice 10 (Flavour)	0.9
Sodium Lauryl Sulphate	1.2
TiO_2	1.0
H_2O	Q.S.

The following tables represent discolouration results upon aging at 120°F (49°C) of the dental creams of Example 1 unless otherwise specified, both unflavoured and containing cinnamic aldehyde (CA) flavourant per se and with specific terpenes or sesquiterpenes containing a trisubstituted double bond or propylene glycol or dipropylene glycol to prevent or reduce the discolouration caused by the cinnamic aldehyde ingredient.

The b values in the tables represent the dental cream yellowing measured on the Colorgard reflectometer and the Δb value represents the increase in yellowing from the unaged and unflavoured sample which is the zero b control.

TABLE 1

Dental Cream Discolouration Studies

120°F (49°C) Aging in Dental Cream of Example 1A

	Control		*3 wks*		*4 wks*		*5 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment I								
0.5% CA							5.2	+2.5
							5.5	+2.8
0.5% CA + 0.5% Limonene							5.2	+2.5
							5.6	+2.9
Unflavoured	2.7						2.9	+0.2

	Control		*6 wks*		*7 wks*		*9 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment I								
0.5% CA			5.7	+3.9			6.6	+4.8
							6.6	+4.8
0.5% CA + 0.5% Limonene			6.0	+4.2			6.7	+4.9
							6.9	+5.1
Unflavoured	2.7		2.7	+0.9			2.9	+1.1

TABLE 1 (continued)

	Control b	Control Δb	3 wks b	3 wks Δb	4 wks b	4 wks Δb	5 wks b	5 wks Δb
Experiment II								
0.5% CA	1.9	+0.2			4.6	+2.6	4.9	+3.1
0.5% CA + 0.5% Eugenol					6.2	+4.2	7.6	+5.8
0.5% CA in Ex. 2A					3.3	+1	3.7	+1.9
0.5% CA + 0.5% Eugenol in Ex. 2A					3.8	+1.9	4.3	+2.5
Unflavoured Ex. 2A	2.0 1.9	1.8 1.9						

	Control b	Control Δb	6 wks b	6 wks Δb	7 wks b	7 wks Δb	9 wks b	9 wks Δb
Experiment II								
0.5% CA					5.7	+3.8	6.4	+4.5
0.5% CA + 0.5% Eugenol					7.7	+5.8	9.5	+7.6
0.5% CA i Ex. 2A					separation		separation	
0.5% CA + 0.5% Eugenol in Ex. 2A					4.8	+2.9	5.6	+3.7
Unflavoured Ex. 2A	2.0 1.9	1.8 1.9						

	Control b	Control Δb	3 wks b	3 wks Δb	4 wks b	4 wks Δb	5 wks b	5 wks Δb
Experiment III								
1% CA			6.6	+3.9	7.6	+5.4		
1% CA + 1% Limonene			4.9	+2.2	5.4	+3.2		
1% CA + 2% Limonene			4.5	+1.8	4.8	+2.6		
Unflavoured	2.7	0						

TABLE 1 (continued)

	Control		*6 wks*		*7 wks*		*9 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment III								
1% CA					9.3	+7.1	10.5	+9
							9.9	+8.9
1% CA + 1% Limonene					6.5	+4.4	7.5	+6
							6.9	+5.4
1% CA + 2% Limonene					5.7	+3.6	6.2	+4.7
							5.8	+4.3
Unflavoured	2.7	0						

	Control		*3 wks*		*4 wks*		*5 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment IV								
1% CA			5.7	+3.6				
1% CA + 1% Ocimene			4.6	+2.5				
1% CA + 2% Ocimene			5.1	+3				
2% Ocimene			3	+0.9				
Unflavoured	2.1		2.1					

	Control		*6 wks*		*7 wks*		*9 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment IV								
1% CA					9.2	+7.3	9.9	+8.1
1% CA + 1% Ocimene					7.3	+5.4	7.7	+5.9
1% CA + 2% Ocimene					7	+5.1	7.7	+5.9
2% Ocimene					3.8	+1.9	3.9	+2.1
Unflavoured	2.1				2.1	+0.2	2	+0.2

TABLE 2

120°F (49°C) Aging in Dental Cream of Example 1A.

	Control		*2 wks*		*3 wks*		*4 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment V								
1% CA					6.7	+4.8		
1% Eugenol					4.1	+2.2		
1% CA + 1% Eugenol					8.1	+6.2		
0.5% CA + 0.5% Eugenol					5.9	+4		
0.9% CA + 0.1% Eugenol					5	+3.1		
1% Spice 10					4.8	+2.9		
10% White Spice #1					3.8	+1.9		
Unflavoured	1.9							

TABLE 2 (continued)

	Control		*6 wks*		*9 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment V						
1% CA			8.4	+6.5	9.6 10.2	+7.9 +8.5
1% Eugenol			4.5	+2.6	4.3	+2.6
1% CA + 1% Eugenol			9.9	+8	10.7	+9
0.5% CA + 0.5% Eugenol			8.1	+6.2	8.9	+7.2
0.9% CA + 0.1% Eugenol			6.6	+4.7	7.2	+5.5
1% Spice 10			6.3	+4.4	6.7 6.4	+5 +4.7
10% White Spice #1			4.6	+2.7	5.0 5.1	+3.3 +3.4
Unflavoured	1.9					

TABLE 2 (continued)

	Control		2 wks		3 wks		4 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment VI								
1% White Spice #2			3.3	+1.2	3.5	+1.7		
Unflavoured	2.1		2.1	0				

	Control		6 wks		9 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment VI						
1% White Spice #2			4.6	+2.9	5.1	+3.2
			4	+2.3		
Unflavoured	2.1		2.2	+0.5	2	+0.1

	Control		2 wks		3 wks		4 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment VII								
0.5 CA +0.5% Eugenol			5.9	+4				
0.5% CA + 0.5% Eugenol + 1% Limonene			4.7	+2.8				
Unflavoured	1.9							

	Control		6 wks		9 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment VII						
0.5 CA +0.5% Eugenol			7.2	+5.3	7.8	+6
			6.9	+5.0	7.8	+6
0.5% CA + 0.5% Eugenol + 1% Limonene			6	+4.1	7	+5.2
			6	+4.1	7.5	+5.7
Unflavoured	1.9					

TABLE 2 (continued)

	Control		2 wks		3 wks		4 wks	
	b	Δ*b*	*b*	Δ*b*	*b*	Δ*b*	*b*	Δ*b*
Experiment VIII								
1% White Spice #1							4.1	+1.9
1% Spice 10							5.6	+3.4
1% Spice 10 + 1% Limonene							4.9	+2.7
1% Spice 11 + 1% Limonene							4.8	+2.6
1% Limonene							2.4	+0.2

	Control		6 wks		9 wks	
	b	Δ*b*	*b*	Δ*b*	*b*	Δ*b*
Experiment VIII						
1% White Spice #1			4.8	+3.0	5.1	+3.5
			4.9	+3.1		
1% Spice 10			5.8	+4.2	5.8	+3.8
			5.6	+4.0	6	+4.4
1% Spice 10 + 1% Limonene			4.8	+3.2	5	+3
			5.2	+3.6	5.4	+3.8
1% Spice 11 + 1% Limonene			5.1	+3.5	5.3	+3.7
			5.4	+3.8		
1% Limonene			2.3	+0.5	1.9	+0.3

TABLE 3

120°F (49°C) Aging in Dental Cream of Example 1A

	Control		*1 wks*		*2 wks*		*3 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment IX								
1% CA			4.5	+2.5			7.2	+5.1
1% CA + 0.25% Limonene							6.1	+4
1% CA + 0.5% Limonene							5.9	+3.8
1% CA + 0.75% Limonene							5.4	+3.3
1% CA + 1% Limonene							5.3	+3.2
1% CA + 1.5% Limonene							5.0	+2.9
1% CA + 3% Limonene							4.8	+2.7
1% CA + 5% Limonene							4.2	+2.1
Unflavoured	2.1							
1% CA + 1% Caryophyllene			3.3	+1.3			5.3	+3.2

TABLE 3 (continued)

	Control b	Control Δb	6 wks b	6 wks Δb	9 wks b	9 wks Δb
Experiment IX						
1% CA			10.5	+8.9	11.1	+9.2
1% CA + 0.25% Limonene			7.7	+6.1	8.5	+6.6
1% CA + 0.5% Limonene			6.9	+5.3	8.3	+6.4
1% CA + 0.75% Limonene			6.9	+5.3	7.8	+5.9
1% CA + 1% Limonene			6.5	+4.9	7.9	+6
1% CA + 1.5% Limonene			6.6	+5.0	6.7	+4.8
1% CA + 3% Limonene			5.3	+3.7	6.2	+4.3
1% CA + 5% Limonene			5.0	+3.4	5.7	+3.8
Unflavoured	2.1					
1% CA + 1% Caryophyllene			6.9	+5.3	7.9	+6

	Control b	Control Δb	1 wks b	1 wks Δb	2 wks b	2 wks Δb	3 wks b	3 wks Δb
Experiment X								
Example 4	1.5				1.8	+0.3	1.8	
Example 4							1.8	−0.2
Example 1A	2.3				2.6	+0.3		
Example 1A							2.5	+0.5
Example 2 Unflavoured	1.6	−0.3					1.7	−0.3
Example 1 Unflavoured	1.9						2.1	+0.1
Example 5 Unflavoured	1.5	−0.4					1.9	−0.1

TABLE 3 (continued)

	Control		6 wks		9 wks	
	b	Δ*b*	*b*	Δ*b*	*b*	Δ*b*
Experiment X						
Example 4	1.5		2.1	+0.4	2.1	+0.2
Example 4			1.6		1.8	−0.1
Example 1A	2.3		2.7	+1	3.0	+1.1
Example 1A			2.3	+0.7	2.3	+0.4
Example 2 Unflavoured	1.6	−0.3			1.5	−0.4
Example 1 Unflavoured	1.9				1.9	
Example 5 Unflavoured	1.5	−0.4			1.8	−0.1

	Control		1 wks		2 wks		3 wks	
	b	Δ*b*	*b*	Δ*b*	*b*	Δ*b*	*b*	Δ*b*
Experiment XI								
1% White Spice 11 + 1% Limonene in Example 5	1.9		2.9	+1.2			4.6	+2.9
			2.9	+1.2			4.5	+2.8
0.5% CA	2.3	+0.1	3.1	+1.4			4.5	+2.9

	Control		6 wks		9 wks	
	b	Δ*b*	*b*	Δ*b*	*b*	Δ*b*
Experiment XI						
1% White Spice 11 + 1% Limonene in Example 5	1.9		5.3	+3.7	5.5	+3.6
			5.2	+3.6	5.4	+3.5
0.5% CA	2.3	+0.1	6.1	+4.5	6.0	+4.1

TABLE 4

120°F (49 °C) Aging in Dental Cream of Example 1A

	Control		*1 wks*		*3 wks*		*5 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XII								
1% CA in Ex. 1A pH 4.9			3.1	+1.3	6.3	+4.5		
1% CA in Ex. 1A pH 6.9			4	+2.2	7	+5.2		
Ex. 1A Unflavoured pH 4.9			1.6		1.8			
Ex. 1A Unflavoured pH 6.9			1.8					
Ex. 2A Unflavoured	1.6							

	Control		*6 wks*		*9 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XII						
1% CA in Ex. 1A pH 4.9			7.4	+5.5	7.2	+4.8
1% CA in Ex. 1A pH 6.9			8.9	+7	8.3	+5.9
Ex. 1A Unflavoured pH 4.9			1.9		2.4	
Ex. 1A Unflavoured pH 6.9			1.9		2.2	
Ex. 2A Unflavoured	1.6					

TABLE 4 (continued)

	Control		1 wks		3 wks		5 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XIII								
0.8% Spice 12 + 0.5% TiO_2 + 0.1% Limonene					2.9	+1.1	3.6	+1.9
Above at pH 5.2 (Citric Acid)					4.9	+3.1	5.3	+3.6
Above at pH 5.1 (H_3PO_4)					4.7	+2.9	5	+3.3
Above at pH 6.2 (H_3PO_4)					4.4	+2.6	4.9	+3.2
Above at pH 5.8 (Citric)					4.7	+2.9	5.2	+3.5
1% Spice 10 + 0.5% TiO_2 + 1% Limonene			2.7	+0.9	3.8 3.6	+2.1 +2.0	4.2	+2.5
Above at pH 5.2 (Citric Acid)			2.6	+0.8	3.5	+1.9	3.8	+2.1
Above at pH 5.1 (H_3PO_4)			2.8	+1.0	3.7 3.2	+2 +1.6	4.3	+2.6
Above at pH 5.8 (Citric)			2.8	+1	3.7	+2.1	4.1	+2.4
Above at pH 6.2 (H_3PO_4)			2.8	+1	3.8	+2.2	4.1	+2.4

TABLE 4 (continued)

	Control		6 wks		9 wks	
	b	Δb	b	Δb	b	Δb
Experiment XIII						
0.8% Spice 12 + 0.5% TiO_2 + 0.1% Limonene					4.9	+2.8
Above at pH 5.2 (Citric Acid)					6.1	+4.0
Above at pH 5.1 (H_3PO_4)						
Above at pH 6.2 (H_3PO_4)						
Above at pH 5.8 (Citric)					5.7	+3.6
1% Spice 10 + 0.5% TiO_2 + 1% Limonene					4.7	+2.6
Above at pH 5.2 (Citric Acid)					4.6	+2.5
Above at pH 5.1 (H_3PO_4)					5.6	+2.5
Above at pH 5.8 (Citric)					5.3	+3.2
Above at pH 6.2 (H_3PO_4)					4.6	+2.5

TABLE 4 (continued)

	Control		1 wks		3 wks		5 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XIV								
1% CA in Ex. 2A					5.2	+3.5		
1% CA + 1% Limonene in Ex. 2A					4.2	+2.5		
Duplicate Sample					4.4	+2.7		
1% Citral					4.9	+3.2		
1% Citral + 1% Limonene					3.7	+2.0		
1% CA + 0.5% TiO_2 pH 5.6					5.2	+3.5		
1% CA + 1% Limonene + 0.5% TiO_2 pH 5.6					4.1	+2.4		
0.8% Spice 12 + 0.5% TiO_2 pH 5.6					4.3	+2.7		
0.8% Spice 12 + 0.1% Limonene + 0.5% TiO_2 pH 5.6					4.2	+2.6		

TABLE 4 (continued)

	Control		6 wks		9 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XIV						
1% CA in Ex. 2A			6.9	+4.7	7.1	+5.3
1% CA + 1% Limonene in Ex. 2A			5.2	+3.0	5.8	+4.0
Duplicate Sample			5.2	+3.0	5.8	+4.0
1% Citral			5.4	+3.2	6.2	+4.4
1% Citral + 1% Limonene			5.4	+2.1	4.8	+3.0
1% CA + 0.5% TiO_2 pH 5.6			6.9	+4.7	6.7	+4.9
1% CA + 1% Limonene + 0.5% TiO_2 pH 5.6			5.1	+2.9	6.1	+4.5
0.8% Spice 12 + 0.5% TiO_2 pH 5.6			5.2	+3.0	5.7	+3.9
0.8% Spice 12 + 0.1% Limonene + 0.5% TiO_2 pH 5.6			5.3	+3.1	5.9	+4.1

TABLE 5

120°F (49°C) Aging in Dental Cream of Example 1b

	1 wk		3 wks		6 wks	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XV						
1% CA in Ex. 8	2.3	+0.3	3.8	+1.8	5.1	+3.4
1% CA + 1% Limonene in Ex. 8	1.7	+0	3.3	+1.3	4.6	+2.9
1% CA + 10% Propylene Glycol	4.0	+1.8	5.0	+3.0	7.1	+5.4
1% CA + 36% Propylene Glycol + 63% Dical phosphate	2.0	+0	1.8	+0	Sample solidified	

TABLE 5 (continued)

	1 wk		*3 wks*		*6 wks*	
	b	*Δb*	*b*	*Δb*	*b*	*Δb*
Experiment XVI						
1% CA	5.1	+3.2	12.6	+10.4	10.4	+6.7
1% CA + 1% Propylene Glycol	5.2	+3.3	9.6	+7.4	4.8	+4.3
1% CA + 1% Dipropylene Glycol	4.5	+2.6	8.6	+6.4	6.4	+2.7
1% CA + 5% Propylene Glycol	4.9	+3.0	8.3 9.1	+6.5	6.6	+2.9
1% CA + 5% Dipropylene Glycol	4.4	+2.5	8.0	+5.8	5.0	+1.3
1% CA + 35% Dipropylene Glycol + 64% Dical Phosphate	1.8	+0	2.4	+0.2	2.9	+0
1% Spice 10	3.9 3.9	+2.1 +2.1	5.7 5.8	+3.6 +3.7	5.7 5.6	+3.9 +3.8
1% Spice 10 + 5% Propylene Glycol	3.7	+1.9	5.5	+3.4	5.8	+4.0
1% Spice 10 + 5% Propylene Glycol +1% Limonene	3.9	+2.1	5.8	+3.7	5.9	+4.1
1% Spice 10 + 5% Propylene Glycol + 1% TiO_2; pH 5.1	2.4 2.7	+0.6 +0.9	3.9 3.7	+1.8 +1.6	-	
Experiment XVIII						
0.9% Spice 10	3.9	+1.7	6.4	+4.0	6.5	+4.7
0.9% Spice 10 in Ex. 9	3.3	+1.1	4.7	+2.3	4.5	+2.7
Experiment XIX						
0.9% Spice 10 in Ex. 9 + 1% TiO_2	2.8	+0.7	2.7	−0	-	

Tables 1 to 4 inclusive disclose formulations containing a variety of flavourants containing cinnamic aldehyde and citral which yellow upon aging, and the reduction of the said yellowing by the addition of limonene or other terpenes and sesquiterpenes characterized by trisubstituted double bonds. The adjustment of the pH to about 6 and the addition of TiO_2 further reduce the yellowing of these flavour-containing formulations.

Dental cream yellowing was measured instrumentally on the Colorgard reflectometer. Data reported on the following tables are + Δb values (yellow scale) and represent the increase in yellow over unflavoured and unaged dental cream which was taken as a zero −b control. Readings taken at 3 wks, 6 and 9 wks at 120°F (49°C) are thought to approximate 1 year, 2 years and 3 years at room temperature. It is approximated that a Δb value of 2 to 3 is the range of marginal acceptability, as a Δb of 2 is visually a slight off white, and a Δb of 4 is a slight yellow-tan.

TABLE 6

Cinnamic Aldehyde Discolouration in Dental Cream (Ex. 1)

A. Influence of Chemicals with Trisubstituted Double Bonds.

	Aging at 120°F (49°C); Δb-values		
	3 wks	*6 wks*	*9 wks*
1.0% Cinnamic Aldehyde (CA)	4.5	7.5	8.0
1.0% CA + 1.0% Limonene	2.9	4.9	5.8
1.0% CA + 1.0% Ocimeme	2.5	5.4	5.9
1.0% CA + 1.0% Caryophyllene	3.2	5.3	6.0
1.0% CA + 1.0% Citronellyl Acetate	3.6	4.2	5.4

B. Influence of pH.

1.0% CA pH 5.0 (Citric Acid)	4.25	5.5	5.1
1.0% CA pH 6.9 to 7.1 (Example 1)	4.5	7.5	8.0
1.0% CA pH 8.5 ($NaHCO_3$)	7.5	10.5	11.2

Reduction improves with increasing amount of terpene as shown with limonene in the drawing.

Although limonene is a mild flavour (orange like) levels beyond 1% would be impractical, and may undesirable because the orange flavour may alter the original cinnamon flavour.

The autoxidation of cinnamic aldehyde is inhibited (interrupted) by the presence of this group of terpenes and sesquiterpenes. Epoxy cinnamic aldehyde formation is prevented when limonene is added to cinnamic aldehyde. Preventing the formation of this epoxide also prevents the formation of the subsequent dienals. It was demonstrated by analytical studies that the limonene reacts preferentially over cinnamic aldehyde with the percinnamic acid to form 1,2-epoxy limonene. It is believed that the other terpenes (2, 3, 4 and 5) form similar epoxides by virtue of the trisubstituted double bond. Trisubstituted double bonds are known to have greater reactivity with peracids than mono- or disubstituted double bonds. Furthermore, cinnamic aldehyde would be expected to have less reactivity toward electrophilic attack of peracids because its double bond is substituted with an electron-withdrawing aldehyde group. Thus, by preventing the formation of the dienals, limonene significantly reduces yellowing. Other terpenes such as eugenol are ineffective in yellowing reduction.

The means for reducing discolouration of cinnamic aldehyde is also applicable to other conjugated unsaturated aldehydes such as citral, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$. Citral is another flavour commonly used in dentifrice compositions.

Yellowing of a liquid mixture of cinnamic aldehyde or citral with a terpene additive was measured on the Gardner tintometer, both when freshly prepared and after aging for 24 hours at 90°C ± 2°. To gram samples were prepared of mixtures of the flavourant and limonene in varying amounts, and the following readings were reported:

		Tintometer	
Cinnamic Aldehyde (%)	*Limonene (%)*	*Fresh*	*Aged*
95	5	4¼	7
90	10	4¼	6¾
75	25	4¼	5
100	0	[a] 4½	[a] 8
50	50	[a] 3¾	[a] 4½

[a] Average of 2 readings.

Citral (%)			
100	0	[b] 1⅓	[b] 3⅔
0	100	[b] 1	-
50	50	[b] 1	[b] 2

[b] Average of 3 readings.

The citral alone and the 50:50 mixture of citral and limonene were additionally aged for:

	4 days	*6 days*	*11 days*
Citral alone	[b] 7	[b] 7⅓	[b] 9⅔
50:50 citral: limonene	[b] 4	[b] 4⅓	[b] 5

The pH of the dental cream is either acid or only slightly alkaline, or preferably a pH of about 5-7.5 as shown in Table 6B. The terpenes are ineffective in reducing yellowing in moderately alkaline medium. At pH 8.5 or above, the peracid anion forms and epoxidation of cinnamic aldehyde proceeds by Michael addition. This type of addition reaction cannot be intercepted by limonene.

It has also now been found that discolouration from low levels of cinnamic aldehyde (a maximum of about 1% by weight) is reduced in the presence of propylene glycol and/or dipropylene glycol. These materials in a 1:1 weight ratio with cinnamic aldehyde are effective in preventing nearly all yellowing on aging in glass. However, in dental cream at levels of 1-5% they showed only slight reduction of yellowing from 1% cinnamic aldehyde. Since these glycols are odourless, it is practical to incorporate them in much higher amounts. The substitution of water or of glycerine in dental formulations by propylene glycol or dipropylene glycol is effective in preventing the yellowing of flavours containing cinnamic aldehyde or citral. When a non-aqueous paste is formulated by replacing the water with either glycol, no discolouration is observed. Also, the replacement of the 22% glycerine in a dental cream by propylene glycol significantly reduced yellowing.

The mechanism of the glycol effect is believed to involve acetal and hemi-acetal formation/complexation. The glycols are believed to be effective by complexing the aldehydes through acetal formation. Since aldehydes are involved in four different phases of the formation mechanism (Figure I), reaction with glycol would significantly interfere with dienal generation. Analysis of the aged 1:1 CA/propylene glycol sample showed appreciable acetal formation with some hemi-acetal. This reversible reaction does have the problem of consuming some of the cinnamic aldehyde. In practice, the cinnamic aldehyde may have to be increased to compensate for this loss.

The autoxidation of cinnamic aldehyde is inhibited (interrupted) by the presence of the propylene glycol due to the formation of glycol acetals which form rapidly at room temperature, and increase with time. This prevents the formation of the dienals which are responsible for the yellowing upon aging.

This means for reducing discolouration of cinnamic aldehyde is also applicable to other conjugated unsaturated aldehydes such as citral, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$. Citral is another flavour commonly used in dentifrice compositions.

Yellowing of a liquid mixture of cinnamic aldehyde with propylene glycol or dipropylene glycol was measured on the Gardner tintometer, both when freshly prepared and after aging for 24 hours in a vial at 90°C (I), and also at 50°C for 48 hours (II), and passing oxygen over the samples initially for 5 seconds. Samples were prepared of mixtures of cinnamic aldehyde and the said glycols, cinnamic aldehyde and glycerine and cinnamic aldehyde per se and the following readings were reported:

	I Tintometer	
	Fresh	*Aged*
Cinnamic Aldehyde (CA)	4	11
50/50 CA + Glycerine	3; 4	~ 11'
50/50 CA + Propylene Glycol	3	7; 7=7
50/50 CA + Dipropylene Glycol	3	10; 8; 9=9

II

Cinnamic Aldehyde	4.5	7
50/50 CA/Propylene Glycol	3.5	4.5

'Glycerine and CA formed two layers. The glycerine layer (bottom) remained water-white, while the upper layer of CA darkened.

It is noted that the propylene glycol mixture is slightly less dark than the dipropylene glycol mixture, but considerably lighter than the cinnamic aldehyde alone.

It is essential that the pH of the dental cream is either acid or neutral, preferably a pH of about 5-7.5 as shown in Table 7. At pH 8.5 or above, the peracid anion forms and epoxidation of cinnamic aldehyde proceeds by Michael addition. This type of addition reaction cannot be intercepted by propylene glycol.

Dental cream yellowing was measured instrumentally on the Colorgard reflectometer. Data reported on the following tables are $+\Delta b$ values (yellow scale) and represent the increase in yellow over unflavoured and unaged dental cream which was taken as a zero $-b$ control. Readings taken at 3, 6 and 9 weeks at 120°F (49°C) are thought to approximate 1 year, 2 years and 3 years at room temperature. It is approximated that a Δb value of 2 to 3 is the range of marginal acceptibility, as a Δb of 2 is visually a slight off white, and a Δb of 4 is a slight yellow-tan.

TABLE 7

Cinnamic Aldehyde Discolouration in Dental Cream (Ex. 1)

Influence of pH

	Aging at 120°F (49°C): Δb− values		
	3 wks	*6 wks*	*9 wks*
1% CA pH 5.0 (Citric Acid)	4.25	5.5	5.1
1% CA pH 6.9 to 7.1 (Example 1)	4.5	7.5	8.0
1% CA pH 8.5 ($NaHCO_3$)	7.5	10.5	11.2

It is also essential that the dentifrice be free of oxidizing agents such as hydrogen peroxide or salts delivering hydrogen peroxide such as sodium perborate, peracids and salts of peracids. The presence of the salt oxidizing agents would interfere with the preferential reaction of the terpene with the percinnamic acid in the formation of the 1,2-epoxy limonene as well as with the preferential reaction of the glycol with cinnamic aldehyde in the formation of the glycol acetals. As discussed with reference to the necessity of maintaining an acid to neutral pH in the dental vehicle, the presence of the peracid anion proceeds to epoxidation of cinnamic aldehyde by Michael addition.

Experiments with various dental bases showed that discolouration of cinnamic aldehyde in Example 2 was approximately half that of Example 1. Also the discolouration in a bicarbonate base gave a very intense yellow. These differences were identified as being due to pH differences and also to the presence of TiO_2 as shown:

	pH	*TiO_2*
Example 1	6.9 to 7.1	0
Example 2	6.15	0.5%

Lowering the pH of Example 1 through the addition of either citric or phosphoric acid reduced yellowing (Table 6B). Increasing pH to 8.5 by adding $NaHCO_3$ significantly increased yellowing. It is noted that the addition of limonene had no effect on reducing the yellowing in the $NaHCO_3$ base (pH 8.5).

These observations are consistent with the autoxidation mechanism outlined. The peracid anion is formed at a pH 8.5 and epoxidation proceeds more rapidly by Michael Addition. Limonene and the other terpenes and sesquiterpenes with trisubstituted olefins are unreactive to nucleophilic addition and thus cannot scavenge the peroxide anion. Peracids are substantially weaker than the corresponding carboxylic acid. The pKa of percinnamic acid is estimated to be 7.5. In a neutral base, both free acid and anion would be present. By lowering the pH the reactions due to the anion addition would be prevented.

As noted with the Example 1 vs. Example 2 comparison, the presence of TiO_2 provides a reduction of yellowing both visually and instrumentally. Based on a number of comparisons with and without TiO_2, a Δb reduction of 1.0 is observed with 1% TiO_2 and 0.5 with 0.5% TiO_2.

An optionally desirable additive which assists in the reduction of cinnamic aldehyde yellowing in dental formulations is titanium dioxide (TiO_2) in minor amounts of about 0.5-1% by weight. Table 8 shows the effectiveness of limonene and of propylene glycol in reducing yellowing in dental creams containing several cinnamic aldehyde containing flavours in the presence and absence of TiO_2.

TABLE 8

Flavour Discolouration in Dental Cream (Example 1)

Flavour				
Cinnamic Aldehyde (CA)	*3 wks*	*6 wks*	*9 wks*	
1% CA	4.5	7.5	8.0	
1% CA + 1% Limonene + 0.5% TiO_2; pH 5.6	2.4	2.9	4.5	
Spice 10 (S10)[1]				
1% S10	3.0	4.2	4.6	
1% S10 + 1% Limonene + 0.5% TiO_2	1.9	2.3	2.6	
Spice 12 (12S)[2]	1 wk	3 wks	6 wks	9wks
0.8% 12S	1	2.7	4.0	4.6
0.8% 12S + 0.1% Limonene	1	2.1	3.2	3.9
0.8% 12S + 0.1% Limonene + 1% TiO_2	-	1.1	2.3	2.6
0.8% 12S + 0.5% Limonene + 1% TiO_2	-	0.7	2.0	2.5
0.8% 12S + 0.25% Limonene	0.9	2.0	3.0	3.5
0.8% 12S + 0.5% TiO_2	-	1.5	2.9	3.1

	1 wk	3 wks	6 wks	9wks
Spice 12 (12S)[2]				
0.8% 12S + 0.1% Limonene + 0.5% TiO_2	-	1.5	-	2.8
0.8% 12S + 0.1% Limonene + 0.5% TiO_2; pH 5.2 (Citric Acid)	-	3.1	-	4.0
0.8% 12S + 0.25% Limonene + 0.5% TiO_2	-	1.5	-	-
0.8% 12S + 0.25% Limonene + 1% TiO_2	-	1.0	-	-
1% CA + 35% Dipropylene Glycol or Propylene Glycol + 64% Dicalcium Phosphate Dihydrate	-	0.2	-	-
Spice 10 (S10)[1]				
1% S10		3.0	4.2	4.6
1% S10 (Glycerine replaced by Propylene Glycol)		2.3	2.7	-
1% S10 (Glycerine replaced by Propylene Glycol) + 1% TiO_2		0.7	-	-

Notes on Table 8
[1]Spice 10 Flavour contains 55% cinnamic aldehyde.
[2]Spice 12 Flavour contains 15% cinnamic aldehyde

Other flavour compositions containing cinnamic aldehyde include:
White Spice 1 - contains 20% cinnamic aldehyde.
White Spice 2 - contains 25% cinnamic aldehyde.
Spice 11 Flavour- contains 55% cinnamic aldehyde.

The cinnamic aldehyde flavour compositions may be completed to 100% with flavour components such as methanol, eugenol, peppermint, spearmint, clove, anethole, methylsalicylate, vanillin and the like in various mixtures. Menthol and eugenol are not involved in the yellowing of the dental formulations.

By blending cinnamic aldehyde with limonene or other terpenes, incorporating TiO_2 and reducing pH, high levels of cinnamic aldehyde may be acceptable.

By blending cinnamic aldehyde with propylene glycol or dipropylene glycol, incorporating TiO_2 and reducing pH, high levels of cinnamic aldehyde also may be acceptable. This can readily be accomplished by replacing the glycerine or the water with propylene glycol, in the dentifrice formulation.

The flavours with cinnamic aldehyde, generally in amount of at least about 5% of the complete flavour, such as Spice 10 or Spice 12, discolour in white dental cream. If the dental cream is coloured green, yellowing is not visually evident.

With Spice 10 flavour, the addition of 1% limonene and 0.5% TiO_2 reduced discolouration to a marginally acceptable range. This addition alters the original flavour but should be useful in achieving similar flavours. In this case 1% TiO_2 and the use of caryophyllene (a spice flavour) with limonene might be preferred.

With Spice 12 flavour the amount of yellowing exceeds that expected from the 15% cinnamic aldehyde content. Interactions due to other components contribute to the discolouration. If this flavour were required for a white paste the addition of only 0.1% limonene and 1% TiO_2 would achieve significant colour improvements and only slightly change the flavour.

CLAIMS

1. A dentifrice formulation having improved stability against discolouration upon aging comprising an unsaturated aldehyde flavourant selected from the group consisting of cinnamic aldehyde and citral which is subject to discolouration with aging, and about 0.1-5% by weight of (1) at least one terpene or sesquiterpene containing trisubstituted double bonds as the discolouration inhibitor, or (2) propylene glycol, dipropylene glycol or a mixture thereof in a dental vehicle free of oxidizing agents and having a pH below 8.5.

2. A dentifrice as claimed in Claim 1, in which the discolouration inhibitor is the said at least one terpene or sesquiterpene.

3. A dentifrice as claimed in Claim 2, in which the amount of the said aldehyde flavourant to terpene is in a 1:1 weight ratio.

4. A dentifrice as claimed in Claim 2 or Claim 3, in which the discolouration inhibitor is limonene, essential oils rich in limonene, ocimene, caryophyllene, cloves sesquiterpenes, myrcene, terpene derivatives thereof, and mixtures thereof.

5. A dentifrice as claimed in Claim 1, in which the discolouration inhibitor is the said propylene glycol, dipropylene glycol or mixture thereof.

6. A dentifrice as claimed in Claim 5, in which the discolouration inhibitor constitutes about 10-45% by weight of the formulations.

7. A dentifrice as claimed in any one of Claims 1 to 6, in which the said flavourant constitutes about 0.1-1% by weight of the formulation.

8. A dentifrice as claimed in any one of Claims 1 to 7, in which the dentifrice is a dental vehicle having a pH of about 5 to 7.5.

9. A dentifrice as claimed in any one of Claims 1 to 8, in which the dental vehicle is an anhydrous dental cream.

10. A dentifrice as claimed in any one of Claims 1 to 8, in which the dental vehicle is an aqueous dental cream.

11. A dentifrice as claimed in any one of Claims 1 to 10, in which the dentifrice is a white colour stabilized dental cream.

12. A dentifrice as claimed in Claim 2, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 1% limonene colour stabilizer.

13. A dental cream as claimed in Claim 2, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 1% ocimene colour stabilizer.

14. A dental cream as claimed in Claim 2, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 1% carophyllene colour stabilizer.

15. A dental cream as claimed in Claim 2, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 1% citronellyl acetate colour stabilizer.

16. A dental cream as claimed in Claim 2, of a white colour dental cream and containing 1% citral flavour and 1% limonene colour stabilizer.

17. A dentifrice as claimed in any one of Claims 1 to 16, which additionally contains about 0.5-1% by weight of titanium dioxide.

18. A dentifrice as claimed in any one of Claims 1 to 77 in the form of a dental cream containing about 20-75% by weight of a water insoluble polishing agent.

19. A dentifrice as claimed in any one of Claims 1 to 8, in which the dentifrice is a white colour stabilized mouthwash.

20. A mouthwash as claimed in Claim 19, containing 0.1-0.5% by weight of a flavour composition containing cinnamic aldehyde or citral.

21. A dentifrice as claimed in any one of Claims 1 to 20, containing about 0.05-5% surfactant.

22. A dentifrice as claimed in any one of Claims 1 to 20, in the form of a dental cream containing a liquid content of about 20-75% by weight of the composition.

23. A dentifrice as claimed in any one of Claims 1 to 20, in the form of a mouthwash containing a liquid content of about 90-89% by weight of the composition.

24. A dental cream as claimed in Claim 4 or Claim 5, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 22% propylene glycol as discolouration inhibitor.

25. A dental cream as claimed in Claim 4 or Claim 5, of a white colour dental cream and containing 1% cinnamic aldehyde flavour and 35% dipropylene glycol as discolouration inhibitor.

26. A dental cream as claimed in Claims 4, 5, 24, or 25, additionally containing about 0.5-1% by weight of titanium dioxide.

27. An anhydrous dental cream as claimed in Claim 9, containing 1% cinnamic aldehyde flavour and 43% propylene glycol.

28. An anhydrous dental cream as claimed in Claim 9, containing 1% cinnamic aldehyde flavour and 22% propylene glycol and 1% titanium dioxide.

29. A mouthwash as claimed in Claim 19, containing 10-15% propylene glycol and 0.1-0.5% cinnamic aldehyde.

30. A mouthwash as claimed in Claim 29, which is anhydrous.

31. A dentifrice as claimed in Claim 1, substantially as specifically described herein with reference to the accompanying examples.

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